

## English Language Machine Translation JP 2004-230280

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### Notes:

1. Untranslatable words are replaced with asterisks (\*\*\*\*\*).
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## CLAIM + DETAILED DESCRIPTION

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[Claim(s)]

[Claim 1]

It processes in the aqueous solution which contains hydrogen peroxide or ozone after processing a polyvinylidene fluoride system resin porous membrane by a base. The manufacture method of the hydrophilic polyvinylidene fluoride system resin porous membrane characterized by processing in the aqueous solution containing at least one kind of salt furthermore chosen from a perchlorate, a perbromic acid salt, and periodate.

[Claim 2]

The manufacture method of a hydrophilic polyvinylidene fluoride system resin porous membrane according to claim 1 that a base is at least one sort chosen from alkali metal hydroxide, an alkaline earth metal hydroxide, and a tertiary amine compound.

[Claim 3]

The hydrophilic polyvinylidene fluoride system resin porous membrane obtained by the manufacture method according to claim 1 or 2.

[Claim 4]

The porous membrane module which was accommodated in the casing equipped with the undiluted solution inflow mouth and the permeate liquid tap hole, and its casing and which has the hydrophilic polyvinylidene fluoride system resin porous membrane obtained by the manufacture method according to claim 1 or 2.

[Claim 5]

Liquid separation equipment which has the permeate liquid suction means prepared in the downstream of a porous membrane module according to claim 4, and the undiluted solution force means prepared in the upstream of this porous membrane module or this porous membrane module.

[Claim 6]

The fresh-water-generation method of obtaining permeated water from raw water using liquid separation equipment according to claim 5.

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to the suitable porous membrane for water treatment, such as potable water manufacture, water purification treatment, and waste water treatment, and the food-stuff-industry field.

[0002]

[Description of the Prior Art]

The porous membrane is used in recent years in various directions, such as the water treatment fields, such as potable water manufacture, water purification treatment, and waste water treatment, and the food-stuff-industry field. In the water treatment fields, such as potable water manufacture, water purification treatment, and waste water treatment, in order that a porous membrane may remove an underwater impurity as substitution of the conventional sand filtration and coagulation sedimentation process, it is used increasingly. Moreover, in the food-stuff-industry field, the porous membrane is used for the purpose of separation removal of the yeast used for fermentation, or concentration of a liquid.

[0003]

Since the porous membrane used variously as mentioned above has the large amount of treated water in the water treatment fields, such as water purification treatment and waste water treatment, improvement in water penetration performance is called for. If the water penetration performance is excellent, since it becomes possible to reduce a membrane area and equipment becomes compact, the cost of equipment can be cut down, and it is advantageous also from a point of film exchange expense or installation area.

[0004]

Moreover, in water purification treatment, for sterilization of permeated water, or the purpose of bio-fouling prevention of a film, in order to add germicides, such as sodium hypochlorite, into a membrane module portion or for an acid, an alkali, chlorine, a surface active agent, etc. to wash the film itself, a porous membrane is asked for medicine-proof performance.

[0005]

Furthermore, receive chlorine, such as *Cryptosporidium* originating in the feces and urine of livestock etc., in tap water manufacture. A tolerant pathogenic microorganism cannot process in a water purification plant, and since the accident mixed in treated water is actualizing from the 1990s, in order to prevent such an accident, sufficient separation characteristics and high physical hardness are demanded of the demarcation membrane as raw water not mixing in treated water.

[0006]

Thus, a porous membrane is asked for separation characteristics, chemical hardness (chemical resistance), the outstanding physical hardness, and outstanding penetration performance.

[0007]

Then, in order to satisfy such demand performances, the porous membrane which used polyvinylidene fluoride system resin has come to be used. However, since polyvinylidene fluoride system resin was hydrophobic resin, hydrophobic substances, such as underwater humus, adhered easily, the porous membrane became dirty, the pore carried out the jam up ball, and there was a problem that water penetration performance falls, or washing by medicine also became dirty and a component was hard to be removed.

[0008]

Then, to introduce a hydrophilic functional group into the principal chain of polyvinylidene fluoride system resin, and to make a porous membrane into hydrophilicity was tried. As a hydrophilic functional group, the hydroxyl group and the carboxyl group were mentioned and various methods were examined.

[0009]

In the patent documents 1, it is a hydroxyl group to an end under base existence. The method on which the polyoxyalkylene which it has is made to act is indicated, the method of carrying out a chemical treatment to the patent documents 2 in the strong alkali solution containing an oxidizing agent is indicated, and the method of carrying out the graft of the monomer containing neutral hydroxyl to the patent documents 3 is indicated. Moreover, the method of carrying out oxidation treatment to the patent documents 4 with the water containing ozone after alkali treatment is indicated.

[0010]

However, although the soil according [ the porous membrane obtained by these hydrophilization methods ] to underwater organic substances, such as humus, is reduced somewhat, it is presumed that the fall of water penetration performance is large and its hydrophilization is inadequate.

[0011]

[Patent documents 1] JP,S53-80378,A

[0012]

[Patent documents 2] JP,S63-172745,A

[0013]

[Patent documents 3] JP,S62-258711,A

[0014]

[Patent documents 4] JP,H5-317663,A

[0015]

[Problem(s) to be Solved by the Invention]

This invention solves the problem which the Prior art mentioned above, and aims at the fall of the water penetration performance by a soil offering few hydrophilic polyvinylidene fluoride system resin porous membranes.

[0016]

[Means for Solving the Problem]

This invention for solving the above-mentioned technical problem [ a polyvinylidene fluoride system resin porous membrane ] It is characterized by the manufacture method of the hydrophilic polyvinylidene fluoride system resin porous membrane which processes in the aqueous solution containing hydrogen peroxide or ozone after processing by a base, and is processed in the aqueous solution containing at least one kind of salt further chosen from a perchlorate, a perbromic acid salt, and periodate. At this time, it is desirable that a base is at least one sort chosen from alkali metal hydroxide, an alkaline earth metal hydroxide, and a tertiary amine compound.

[0017]

And the hydrophilic polyvinylidene fluoride system resin porous membrane obtained by the manufacture method of one of the above is also desirable. Moreover, the porous membrane module which was accommodated in the casing equipped with the undiluted solution inflow mouth and the permeate liquid tap hole and its casing and which has the

hydrophilic polyvinylidene fluoride system resin porous membrane obtained by the manufacture method of one of the above is also desirable. Furthermore, the liquid separation equipment which has the permeate liquid suction means prepared in the downstream of this porous membrane module, and the undiluted solution force means prepared in the upstream of this porous membrane module or this porous membrane module is also desirable. The fresh-water-generation method of obtaining permeated water from raw water using the liquid separation equipment is also a desirable mode.

[0018]

[Embodiment of the Invention]

In the manufacture method of the hydrophilic polyvinylidene fluoride system resin porous membrane of this invention After processing a polyvinylidene fluoride system resin porous membrane by a base, it processes in the aqueous solution containing hydrogen peroxide or ozone, and it processes in the aqueous solution containing at least one kind of salt further chosen from a perchlorate, a perbromic acid salt, and periodate.

[0019]

In this invention, although a porous membrane contains polyvinylidene fluoride system resin, polyvinylidene fluoride system resin is resin containing a vinylidene fluoride homopolymer and/or a vinylidene fluoride copolymer. You may contain two or more kinds of vinylidene fluoride copolymers. The copolymer of the at least one sort and vinylidene fluoride which were chosen from the group which consists of fluoridation vinyl, tetrafluoroethylene, 6 fluoridation propylene, and 3 fluoride-salt-ized ethylene as a vinylidene fluoride copolymer is mentioned.

[0020]

Moreover, although what is necessary is just to choose it suitably with the hardness and water penetration performance of a hollow fiber which are demanded, when the workability to a porous membrane is taken into consideration, it is desirable [ the weight average molecular weight of polyvinylidene fluoride system resin ] that it is within the limits of 50,000-1 million, and also 100,000-450,000. If the viscosity of a resin solution will become high too much if a weight average molecular weight becomes larger than this range, and it becomes smaller than this range, the viscosity of a resin solution will become low too much, and it will become difficult for all to fabricate a porous membrane.

[0021]

A hollow fiber or a flat film is sufficient as the form of the porous membrane of this invention, and it is chosen by the use.

[0022]

In the case of a hollow fiber, it is desirable that an inside diameter designs so that 200 micrometers - 12mm, 120 more micrometers - 15mm, and thickness may become the range of 50 micrometers - 1mm, and 20 more micrometers - 3mm in 150 micrometers - 8mm, 100 more micrometers - 10mm, and an outside diameter. Moreover, although the pole diameter on the surface of inside and outside of a hollow fiber can be freely chosen by a use, it is desirable to design to become the range of 0.005 micrometer (5nm) - 10 micrometers, and 0.008 more micrometer (8nm) - 8 micrometers. The internal structure of a hollow fiber may be the homogeneous structure of having the hole of the same size as a thickness direction, even if it is arbitrary and what is called a macro void exists. Furthermore, polymer could be infiltrated into what coated polymer on it by using as a

support material what knit organic fiber, such as polyester and nylon, glass fiber, a metal fiber, etc. to tubed, and a part of its support material.

[0023]

On the other hand, in the case of a flat film, it is desirable that thickness is within the limits of 10 micrometers - 1mm, and 30 more micrometers - 500 micrometers. It is desirable that the case of a flat film also has in polymer coating or the thickness which may be infiltrated in part and contains this field-like support material in that case within the limits of above-mentioned in the support material of the shape of a field, such as textiles, knitting, and a nonwoven fabric. Moreover, although a surface pole diameter can be freely chosen by a use, it is desirable that it is in the range of 0.005 micrometer (5nm) - 10 micrometers, and 0.008 more micrometer (8nm) - 8 micrometers. The internal structure of a flat film may be the homogeneous structure in which the hole of the same size as a thickness direction opened, even if it is arbitrary and what is called a macro void exists.

[0024]

The porous membrane of above-mentioned this invention is manufactured with either of the following three methods, for example.

[0025]

[ the polymer solution which dissolved I polyvinylidene-fluoride system resin in the good solvent ] The wet solution technique in which make the liquid containing the non solvent of polyvinylidene fluoride system resin contact, and unsymmetrical porous structure is made to form according to non solvent induction phase separation after extruding from a nozzle, or carrying out the cast on a glass plate and fabricating at a temperature quite lower than the fusing point of polyvinylidene fluoride system resin.

[0026]

Fusion kneading of inorganic particles and the organic liquefied object is carried out at 2 polyvinylidene-fluoride system resin. The fusion extraction method which forms porous structure by carrying out cooling solidification after extruding from a nozzle, or pressing with a pressing machine and fabricating at the temperature beyond the fusing point of polyvinylidene fluoride system resin, and extracting an organic liquefied object and inorganic particles after that.

[0027]

It cools, after carrying out the high temperature dissolution at the solvent which cannot dissolve 3 polyvinylidene-fluoride system resin easily at a room temperature, manufacturing a polyvinylidene fluoride system resin solution and breathing out the polyvinylidene fluoride system resin solution from a nozzle, and they are phase separation and the heat-induced phase separation method made to solidify.

[0028]

Process the polyvinylidene fluoride system resin porous membrane obtained as mentioned above in this invention, for example by one base, and it ranks second two. It processes in the aqueous solution containing hydrogen peroxide or ozone, and processes in the aqueous solution containing at least one kind of salt chosen from the group which becomes 3 pans from a perchlorate, a perbromic acid salt, and periodate.

[0029]

[ treatment by the aqueous solution which hydrogen fluoride is desorbed from polyvinylidene fluoride system resin, and contains the hydrogen peroxide or ozone of 2

by base treatment of 1 ] A hydroxyl group and/or a carboxyl group are introduced, the content of a carboxyl group increases by treatment by the aqueous solution containing the perchlorate of further 3 etc., and hydrophilicity increases.

[0030]

As a base which can be used for base treatment Alkali metal hydroxide, such as lithium hydroxide, sodium hydroxide, and potassium hydroxide, Alkaline earth metal hydroxides, such as magnesium hydroxide and a calcium hydroxide, An alkali metal or alkaline earth metal alkoxide, trimethylamine, Triethylamine, 1, 4-diazabicyclo [2.2.2] octane, The 4th class ammonium hydroxides, such as tertiary amine, such as 1, 7-diazabicyclo [5.4.0] 7-undecene, 1, and 8-diazabicyclo [4.3.0] 5-nonene, and tetrabutylammonium hydroxide, can be mentioned.

[0031]

These bases process by independent or the thing of water and an alcohol for which it dissolves in mixed liquor, and a porous membrane is immersed in the solution, or it lets a solution flow to a porous membrane. When letting a solution flow to a porous membrane, it is more effective, if it carries out after using a porous membrane as a module. As an alcohol, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, etc. can be mentioned. When making it the mixed liquor of water and an alcohol, it depends for the ratio of an alcohol and water on the solubility of a base. Although the amount of addition of a base changes with kinds of base Since the physical hardness of a porous membrane will be spoiled if too high [ if too low, a porous membrane cannot be made to fully react, but ], In the case of a hydroxide, it is usually preferably chosen within the limits of 0.005 to 1 regulation 0.001 to 5 \*\*\*\*, and, in the case of a tertiary amine compound, is usually preferably chosen by 0.05 to 5% of within the limits 0.01 to 10%.

[0032]

On the occasion of base treatment, if the temperature of a solution is too low, a porous membrane cannot fully be reacted, but since the physical hardness of a porous membrane will be spoiled if too high, 10 degrees C - 80 degrees C are usually preferably chosen within the limits of 20 degrees C - 60 degrees C.

[0033]

Next, about the aqueous solution containing the hydrogen peroxide or ozone of 2, if the concentration of hydrogen peroxide is too low, it cannot fully react with a porous membrane, but if too high, since it is dangerous, it will usually be preferably chosen by 0.3 to 5% of within the limits 0.1 to 10%. If the temperature of a solution is too low, it cannot fully react a porous membrane, but if too high, since it is dangerous, it will usually be preferably chosen within the limits of 20-40 degrees C 10-50 degrees C. And treatment is performed by a porous membrane being immersed in a hydrogen-peroxide-solution solution, or letting a solution flow to a porous membrane. When letting a solution flow to a porous membrane, it is more effective, if it carries out after using a porous membrane as a module.

[0034]

On the other hand, although it is about treatment by the aqueous solution containing ozone, treatment is performed, letting flow the water which contains immersion or ozone in the water containing ozone for a porous membrane to a porous membrane. From a point of treatment efficiency, latter one is desirable. Moreover, when letting flow the water which contains ozone in a porous membrane, it is still more efficient, if a porous

membrane is used as a module and performed. Time is taken too much, and if the underwater ozone concentration in the case of ozonization is not practical and is too high, since it cannot respond but equipment is specialized, it will usually be preferably chosen within the limits of 0.5-20 ppm 0.1-30 ppm with the usual ozonizer, until it will give hydrophilicity on the surface of a porous membrane, if it is too low. Moreover, it is still more effective if a supersonic wave is used together in the case of ozonization. If the temperature of a solution is too high, the solubility of ozone will become small, and since a rate of reaction will fall if too low, 1-50 degrees C is usually preferably chosen among 10-40 degrees C.

[0035]

And although it is about treatment in the aqueous solution containing at least one kind of salt chosen from the group which consists of the perchlorate, the perbromic acid salt, and periodate of 3, the aqueous solution containing a salt shows the state where dissolved the salt in water and it dissociated to the ion. As a perchlorate, lithium perchlorate, sodium perchlorate, potassium perchlorate, ammonium perchlorate, etc. can be mentioned. As a perbromic acid salt, perbromic acid lithium, perbromic acid sodium, perbromic acid potassium, perbromic acid ammonium, etc. can be mentioned. As periodate, periodic acid lithium, periodic acid sodium, potassium periodate, periodic acid ammonium, etc. can be mentioned.

[0036]

If the concentration of these salts is too low, it cannot fully react a porous membrane, but if too high, since it is dangerous, it will usually be preferably chosen by 0.3 to 5% of within the limits 0.1 to 10%. If the temperature of a solution is too low, it cannot fully react a porous membrane, but if too high, since it is dangerous, it will usually be preferably chosen from 10 degrees C in 20 to 40 degrees C 50 degrees C. Treatment is performed by a porous membrane being immersed in the aqueous solution containing this salt, or letting a solution flow to a porous membrane. When letting a solution flow to a porous membrane, it is more effective, if a porous membrane is used as a module and performed.

[0037]

Even if the porous membrane of this invention pass such a process of 1-3 filters a commercial humic acid aqueous solution continuously, for example, its fall of the water penetration performance accompanying progress of time is small. Furthermore, after carrying out water penetration degradation, water penetration performance is recoverable with what is called a back wash that supplies permeated water to the filtration direction and an opposite direction.

[0038]

In addition, the difficulty of becoming dirty is evaluated as follows. That is, in a hollow fiber-shaped thing, a miniature module with a length of 200mm which consists of four hollow fibers is produced, and the water penetration performance of pure water is measured under the temperature of 25 degrees C, and the condition of filtration differential pressure 16kPa. Next, a predetermined time deed and the permeate flow rate per the unit time are measured for a 20 ppm humic acid aqueous solution by all the external pressure filtration, and the water permeability of unit membrane area (m2) is searched for by carrying out pressure (50kPa) conversion. Permeated water is supplied to a pan for 1 minute by the back-washing pressure power of 150kPa, and the pure water

water penetration performance just behind that is measured. On the other hand, it asks at a flat film-shaped thing by carrying out the operation as a hollow fiber 50mm in diameter which starts circularly and sets to a cylindrical filtration holder that others are the same.

[0039]

The porous membrane of above-mentioned this invention is accommodated in the casing equipped with the undiluted solution inflow mouth, the permeate liquid tap hole, etc., and is used as a porous membrane module. When a porous membrane is a hollow fiber, a porous membrane module bundles two or more hollow fibers, dedicates them to a cylindrical container, fixes both ends or one end by polyurethane, an epoxy resin, etc., fixes the both ends of a hollow fiber to plate-like, and enables it to enable it to collect permeate liquid or to collect permeate liquid. When a porous membrane is a flat film, it rolls round in the shape of a spiral, folding up a flat film in the shape of an envelope around a liquid collecting tube, and dedicates to a cylindrical container, and a flat film arranges to both sides of a liquid collecting plate, the circumference is fixed [ permeate liquid is made to be made, or ] watertight, and it enables it to collect permeate liquid.

[0040]

And a porous membrane module is used as liquid separation equipment which prepares a suction means in the force means or permeate liquid side, and performs fresh water generation to the undiluted solution side at least. A pump may be used as a force means and at least water may use the pressure by a difference. Moreover, what is necessary is just to use a pump and a siphon as a suction means.

[0041]

If this liquid separation equipment is the water treatment field, it can be used by water purification treatment, purification of water, waste water treatment, industrial water manufacture, etc., and will use river water, lake water, ground water, sea water, sewage, wastewater, etc. as processed water.

[0042]

[Example]

The water penetration performance of the porous membrane in a work example and a comparative example was measured as follows.

[0043]

When a porous membrane is a hollow fiber, a miniature module with a length of 200mm which consists of four hollow fibers is produced, under the temperature of 25 degrees C, and the condition of filtration differential pressure 16kPa, the amount of water penetration of pure water is measured, and pressure (50kPa) conversion is carried out ( $Q_0$ , unit =  $\text{m}^3/\text{m}^2\text{andh}$ ). Next, a 20 ppm humic acid (reagent, WAKO PURE CHEMICAL INDUSTRIES LTD. make) aqueous solution is filtered that it seems that it becomes  $2\text{m}^3/\text{m}^2$  by all the external pressure filtration under filtration differential pressure 16kPa and a condition with a temperature of 25 degrees C. Permeated water is supplied to a pan for 1 minute by the back-washing pressure power of 150kPa, and the amount of pure water water penetration just behind that is measured ( $Q_1$ ).  $A=Q_1/Q_0$  are used as an index of hydrophilization.

[0044]

When a porous membrane is a flat film, the operation as a hollow fiber 50mm in diameter which starts circularly and sets to a cylindrical filtration holder that others are the same is carried out.



<Work example 1>

The vinylidene fluoride homopolymer of weight average molecular weight 417,000 was dissolved in N, N dimethylformamide at the temperature of 80 degrees C so that it might become 20 weight %. While making the mixed solvent which consists of N, N dimethylformamide / water = 80/20 (weight %) considering this resin solution as a hollow part formation liquid accompany After breathing out from the 60-degree C nozzle and passing about 5cm dry type part, it introduced into the coagulation bath with a temperature of 30 degrees C which consists of N, N dimethylformamide / water 20/80 (weight %), and solidified. The obtained hollow fiber was 0.5mm in 0.8mm of outside diameters, and inside diameter. 50kPa and the amount of pure water water penetration at 25 degrees C were 0.055m<sup>3</sup>/m<sup>2</sup>andh.

[0045]

The obtained hollow fiber was immersed in the 30-degree C 0.01 regulation sodium hydroxide aqueous solution for 2 hours, and it was immersed in hydrogen peroxide solution at 30 degrees C after-flush 3weight % for 24 hours. It was further immersed in the lithium perchlorate aqueous solution 1weight % after the flush for 4 hours. 50kPa of the obtained hollow fiber and the amount of pure water water penetration at 25 degrees C were 0.070m<sup>3</sup>/m<sup>2</sup>andh (Q0).

[0046]

Under the temperature of 25 degrees C, and the condition of filtration differential pressure 16kPa, that it seems that it becomes 2m<sup>3</sup>/m<sup>2</sup>, it filtered and the back wash of the humic acid aqueous solution was carried out. The amounts of pure water water penetration were 0.065m<sup>3</sup>/m<sup>2</sup>andh (Q1). In addition, the evaluation result was summarized in Table 1.

[0047]

[Table 1]

实施例	Q0 ( $\text{m}^3/\text{m}^2 \cdot \text{h}$ )	Q1 ( $\text{m}^3/\text{m}^2 \cdot \text{h}$ )	$A = Q1/Q0$
实施例 1	0.070	0.065	0.93
实施例 2	0.074	0.071	0.96
实施例 3	1.62	1.55	0.96
实施例 4	1.71	1.61	0.94
实施例 5	7.55	7.22	0.96
实施例 6	7.88	7.35	0.93
比较例 1	0.061	0.030	0.49
比较例 2	0.062	0.033	0.53
比较例 3	1.55	0.82	0.53
比较例 4	1.62	0.88	0.54
比较例 5	7.33	3.45	0.47
比较例 6	7.50	3.52	0.47

[0048]

<Work example 2>

The hollow fiber was replaced with being immersed in hydrogen peroxide solution at 30 degrees C 3weight % for 24 hours, and it was made to be the same as that of a work example 1 except having carried out immersion treatment by underwater [ containing ozone 10ppm / 25-degree C ] for 100 hours. 50kPa of the hollow fiber after treatment by a lithium perchlorate aqueous solution and the amount of pure water water penetration at 25 degrees C were 0.074m<sup>3</sup>/m<sup>2</sup>andh (Q0). Moreover, the amounts of pure water water penetration after humic acid aqueous solution filtration and a back wash were 0.071m<sup>3</sup>/m<sup>2</sup>andh (Q1). The evaluation result was summarized in Table 1.

<Comparative example 1>

It was made to be the same as that of a work example 1 except not having carried out lithium perchlorate aqueous solution treatment. The amounts of pure water water penetration of the hollow fiber washed and measured were 0.061m<sup>3</sup>/m<sup>2</sup>andh after treatment by hydrogen peroxide solution (Q0). The amounts of pure water water penetration after humic acid aqueous solution filtration and a back wash were 0.030m<sup>3</sup>/m<sup>2</sup>andh (Q1). The evaluation result was summarized in Table 1.

<Comparative example 2>

It was made to be the same as that of a work example 2 except not having carried out lithium perchlorate aqueous solution treatment. After processing by underwater [ containing ozone 10ppm ], the amounts of pure water water penetration of the hollow

fiber washed and measured were 0.062m<sup>3</sup>/m<sup>2</sup>andh (Q0). The amounts of pure water water penetration after humic acid aqueous solution filtration and a back wash were 0.033m<sup>3</sup>/m<sup>2</sup>andh (Q1). The evaluation result was summarized in Table 1.

<Work example 3>

The vinylidene fluoride homopolymer of weight average molecular weight 417,000 was dissolved in gamma-butyrolactone at the temperature of 150 degrees C so that it might become 38 weight %. While making the mixed solvent which consists of gamma-butyrolactone / water = 80/20 (weight %) considering this resin solution as a hollow part formation liquid accompany Gamma-butyrolactone/water after breathing out from the 100-degree C nozzle and passing about 2cm dry type part = it introduced into the coagulation bath with a temperature of 15 degrees C which consists of 80/20 (weight %), and solidified. The obtained hollow fiber was 0.8mm in 1.2mm of outside diameters, and inside diameter. 50kPa and the amount of pure water water penetration at 25 degrees C were 1.50m<sup>3</sup>/m<sup>2</sup>andh.

[0049]

The obtained hollow fiber was immersed in the 30-degree C 0.01 regulation sodium hydroxide aqueous solution for 2 hours, and it was immersed in hydrogen peroxide solution at 30 degrees C after-flush 3weight % for 24 hours. It was further immersed in the lithium perchlorate aqueous solution 1weight % after the flush for 4 hours. 50kPa of the obtained hollow fiber and the amount of pure water water penetration at 25 degrees C were 1.62m<sup>3</sup>/m<sup>2</sup>andh (Q0).

[0050]

The amounts of pure water water penetration after humic acid aqueous solution filtration and a back wash were 1.55m<sup>3</sup>/m<sup>2</sup>andh (Q1). The evaluation result was summarized in Table 1.

<Work example 4>

The hollow fiber was replaced with being immersed in hydrogen peroxide solution at 30 degrees C 3weight % for 24 hours, and it was made to be the same as that of a work example 3 except having carried out immersion treatment by underwater [ containing ozone 10ppm / 25-degree C ] for 100 hours. 50kPa of the hollow fiber after treatment by a lithium perchlorate aqueous solution and the amount of pure water water penetration at 25 degrees C were 1.71m<sup>3</sup>/m<sup>2</sup>andh (Q0). The amounts of pure water water penetration after humic acid aqueous solution filtration and a back wash were 1.61m<sup>3</sup>/m<sup>2</sup>andh (Q1). The evaluation result was summarized in Table 1.

<Comparative example 3>

It was made to be the same as that of a work example 3 except not having carried out lithium perchlorate aqueous solution treatment. The amounts of pure water water penetration of the hollow fiber washed and measured were 1.55m<sup>3</sup>/m<sup>2</sup>andh after treatment by hydrogen peroxide solution (Q0). The amounts of pure water water penetration after humic acid aqueous solution filtration and a back wash were 0.82m<sup>3</sup>/m<sup>2</sup>andh (Q1). The evaluation result was summarized in Table 1.

<Comparative example 4>

It was made to be the same as that of a work example 4 except not having carried out lithium perchlorate aqueous solution treatment. After processing by underwater [ containing ozone 10ppm ], the amounts of pure water water penetration of the hollow fiber washed and measured were 1.62m<sup>3</sup>/m<sup>2</sup>andh (Q0). The amounts of pure water water

penetration after humic acid aqueous solution filtration and a back wash were 0.88m<sup>3</sup>/m<sup>2</sup>andh (Q1). The evaluation result was summarized in Table 1. <Work example 5>

13.0 weight % of vinylidene fluoride homopolymers of weight average molecular weight 417,000 and a weight average molecular weight are about 20. 5.5 weight % of 000 polyethylene glycol (PEG), Using respectively 81.5 weight % of N and N-dimethylacetamides (DMAc) as a solvent, these were fully agitated under the temperature of 90 degrees C, and the undiluted solution was obtained. Next, after cooling the above-mentioned undiluted solution at 25 degrees C, a density applies to the nonwoven fabric made from polyester fiber 0.48g/cm<sup>3</sup> and whose thickness are 220 micrometers, and it is immediately immersed for 5 minutes into 25-degree C pure water after spreading, and is immersed in 80 more-degree C hot water 3 times. The thickness of the whole which probed DMAc and PEG and contained the nonwoven fabric of the obtained flat film was 315 micrometers. 50kPa and the amount of pure water water penetration at 25 degrees C were 6.71m<sup>3</sup>/m<sup>2</sup>andh.

[0051]

The obtained flat film was immersed in the 30-degree C 0.01 regulation sodium hydroxide aqueous solution for 2 hours, and it was immersed in hydrogen peroxide solution at 30 degrees C after-flush 3weight % for 24 hours. It was further immersed in the lithium perchlorate aqueous solution 1weight % after the flush for 4 hours. 50kPa of the obtained flat film and the amount of pure water water penetration at 25 degrees C were 7.55m<sup>3</sup>/m<sup>2</sup>andh (Q0).

[0052]

The amounts of pure water water penetration after humic acid aqueous solution filtration and a back wash were 7.22m<sup>3</sup>/m<sup>2</sup>andh (Q1). The evaluation result was summarized in Table 1.

<Work example 6>

The flat film was replaced with being immersed in hydrogen peroxide solution at 30 degrees C 3weight % for 24 hours, and it was made to be the same as that of a work example 5 except having carried out immersion treatment by underwater [ containing ozone 10ppm / 25-degree C ] for 100 hours. 50kPa of the flat film after treatment by a lithium perchlorate aqueous solution and the amount of pure water water penetration at 25 degrees C were 7.88m<sup>3</sup>/m<sup>2</sup>andh (Q0). The amounts of pure water water penetration after humic acid aqueous solution filtration and a back wash were 7.35m<sup>3</sup>/m<sup>2</sup>andh (Q1). The evaluation result was summarized in Table 1.

<Comparative example 5>

It was made to be the same as that of a work example 5 except not having carried out lithium perchlorate aqueous solution treatment. The amounts of pure water water penetration of the flat film washed and measured were 7.33m<sup>3</sup>/m<sup>2</sup>andh after treatment by hydrogen peroxide solution (Q0). The amounts of pure water water penetration after humic acid aqueous solution filtration and a back wash were 3.45m<sup>3</sup>/m<sup>2</sup>andh (Q1). The evaluation result was summarized in Table 1.

<Comparative example 6>

It was made to be the same as that of a work example 6 except not having carried out lithium perchlorate aqueous solution treatment. After processing by underwater [ containing ozone 10ppm ], the amounts of pure water water penetration of the flat film

washed and measured were 7.50m<sup>3</sup>/m<sup>2</sup>andh (Q0).

[0053]

The amounts of pure water water penetration after humic acid aqueous solution filtration and a back wash were 3.52m<sup>3</sup>/m<sup>2</sup>andh (Q1). The evaluation result was summarized in Table 1.

[0054]

[Effect of the Invention]

According to this invention, the small hydrophilic polyvinylidene fluoride system resin porous membrane of the amount fall of water penetration by the soil of organic substances, such as humic acid, can be offered. Since the washing interval of a porous membrane becomes long and becomes long [ a filtration life ] by this, reduction of fresh-water-generation cost is attained.

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[Translation done.]